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U.S. DEPARTMENT OF COMMERCE PATENT AND TRADEMARK OFFICE

ATTORNEY'S DOCKET NUMBER

J342-011 US

U.S. APPLICATION NO. (If known, see 37 CFR 1.5)

10/018175

**TRANSMITTAL LETTER TO THE UNITED STATES
DESIGNATED/ELECTED OFFICE (DO/EO/US)
CONCERNING A FILING UNDER 35 U.S.C. 371**

INTERNATIONAL APPLICATION NO.
PCT/FR00/01636

INTERNATIONAL FILING DATE
June 13, 2000

PRIORITY DATE CLAIMED
June 11, 1999

TITLE OF INVENTION

METHOD FOR PROTECTING METALS AGAINST CORROSION AND NON-POLLUTING REACTIVE COMPOSITION THEREFOR

APPLICANT(S) FOR DO/EO/US

Jacques Pierre POUYFAUCON, Bernard Jean Leon BOUTEVIN and Yves HERVAUD

Applicant herewith submits to the United States Designated/Elected Office (DO/EO/US) the following items and other information:

1. ☒ This is a **FIRST** submission of items concerning a filing under 35 U.S.C. 371.
2. ☐ This is a **SECOND** or **SUBSEQUENT** submission of items concerning a filing under 35 U.S.C. 371.
3. ☒ This is an express request to begin national examination procedures (35 U.S.C. 371(f)). The submission must include items (5), (6), (9) and (21) indicated below.
4. ☐ The US has been elected by the expiration of 19 months from the priority date (Article 31).
5. ☒ A copy of the International Application as filed (35 U.S.C. 371(c)(2))
 - a. ☐ is attached hereto (required only if not communicated by the International Bureau).
 - b. ☒ has been communicated by the International Bureau.
 - c. ☐ is not required, as the application was filed in the United States Receiving Office (RO/US).
6. ☐ An English language translation of the International Application as filed (35 U.S.C. 371(c)(2)).
 - a. ☐ is attached hereto.
 - b. ☐ has been previously submitted under 35 U.S.C. 154(d)(4).
7. ☒ Amendments to the claims of the International Application under PCT Article 19 (35 U.S.C. 371(c)(3))
 - a. ☐ are attached hereto (required only if not communicated by the International Bureau).
 - b. ☐ have been communicated by the International Bureau.
 - c. ☐ have not been made; however, the time limit for making such amendments has NOT expired.
 - d. ☒ have not been made and will not be made.
8. ☐ An English language translation of the amendments to the claims under PCT Article 19 (35 U.S.C. 371 (c)(3)).
9. ☐ An oath or declaration of the inventor(s) (35 U.S.C. 371(c)(4)).
10. ☐ An English language translation of the annexes of the International Preliminary Examination Report under PCT Article 36 (35 U.S.C. 371(c)(5)).

Items 11 to 20 below concern document(s) or information included:

11. ☐ An Information Disclosure Statement under 37 CFR 1.97 and 1.98.
12. ☐ An assignment document for recording. A separate cover sheet in compliance with 37 CFR 3.28 and 3.31 is included.
13. ☐ A FIRST preliminary amendment.
14. ☐ A SECOND or SUBSEQUENT preliminary amendment.
15. ☐ A substitute specification.
16. ☐ A change of power of attorney and/or address letter.
17. ☐ A computer-readable form of the sequence listing in accordance with PCT Rule 13ter.2 and 35 U.S.C. 1.821 - 1.825.
18. ☐ A second copy of the published international application under 35 U.S.C. 154(d)(4).
19. ☐ A second copy of the English language translation of the international application under 35 U.S.C. 154(d)(4).
20. ☒ Other items or information: **International Search Report**

U.S. APPLICATION NO. (if known, see 37 CFR 1.55)

INTERNATIONAL APPLICATION NO.
PCT/FR00/01636ATTORNEY'S DOCKET NUMBER
J342-011 US21. ☒ The following fees are submitted:**BASIC NATIONAL FEE (37 CFR 1.492 (a) (1) - (5)):**

Neither international preliminary examination fee (37 CFR 1.482)
nor international search fee (37 CFR 1.445(a)(2)) paid to USPTO
and International Search Report not prepared by the EPO or JPO \$1000.00

International preliminary examination fee (37 CFR 1.482) not paid to
USPTO but International Search Report prepared by the EPO or JPO \$860.00

International preliminary examination fee (37 CFR 1.482) not paid to USPTO
but international search fee (37 CFR 1.445(a)(2)) paid to USPTO \$710.00

International preliminary examination fee (37 CFR 1.482) paid to USPTO
but all claims did not satisfy provisions of PCT Article 33(1)-(4) \$690.00

International preliminary examination fee (37 CFR 1.482) paid to USPTO
and all claims satisfied provisions of PCT Article 33(1)-(4) \$100.00

ENTER APPROPRIATE BASIC FEE AMOUNT =

CALCULATIONS PTO USE ONLY

\$ 890.00

Surcharge of \$130.00 for furnishing the oath or declaration later than ☐ 20 ☐ 30
months from the earliest claimed priority date (37 CFR 1.492(e)). \$

CLAIMS	NUMBER FILED	NUMBER EXTRA	RATE	\$
Total claims	15 - 20 =		x \$18.00	\$
Independent claims	2 - 3 =		x \$80.00	\$
MULTIPLE DEPENDENT CLAIM(S) (if applicable)			+ \$270.00	\$

TOTAL OF ABOVE CALCULATIONS =

\$ 890.00

☐ Applicant claims small entity status. See 37 CFR 1.27. The fees indicated above
are reduced by 1/2. +

SUBTOTAL =

\$ 890.00

Processing fee of \$130.00 for furnishing the English translation later than ☐ 20 ☐ 30
months from the earliest claimed priority date (37 CFR 1.492(f)). \$

TOTAL NATIONAL FEE =

\$ 890.00

Fee for recording the enclosed assignment (37 CFR 1.21(h)). The assignment must be
accompanied by an appropriate cover sheet (37 CFR 3.28, 3.31). \$40.00 per property +

TOTAL FEES ENCLOSED =

\$ 890.00

Amount to be
refunded:

\$

charged:

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- a. ☒ A check in the amount of \$ 890.00 to cover the above fees is enclosed.
- b. ☐ Please charge my Deposit Account No. _____ in the amount of \$ 890.00 to cover the above fees.
A duplicate copy of this sheet is enclosed.
- c. ☒ The Commissioner is hereby authorized to charge any additional fees which may be required, or credit any
overpayment to Deposit Account No. 14-1431. A duplicate copy of this sheet is enclosed.
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information should not be included on this form. Provide credit card information and authorization on PTO-2038.

NOTE: Where an appropriate time limit under 37 CFR 1.494 or 1.495 has not been met, a petition to revive (37 CFR
1.137 (a) or (b)) must be filed and granted to restore the application to pending status.

SEND ALL CORRESPONDENCE TO:

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VIA EXPRESS MAIL LABEL NO. EV011294773 US

SIGNATURE

Peter C. Michalos

NAME

28,643

REGISTRATION NUMBER

Dated: December 11, 2001

VERIFICATION OF A TRANSLATION

I, the below named translator, hereby declare that:

My name and post office address are as stated below:

That I am knowledgeable in the English language and in the language in which the below identified international document was written, and that I believe the English translation of the attached international document,

WO 00/77101, entitled "Method for protecting metals against corrosion and non-polluting reactive composition therefor"

is a true and complete translation of the above-identified document as filed.

I hereby declare that all statements made herein are true and that all statements made on information and belief are believed to be true; and further that these statements were made with the knowledge that willful false statements and the like so made are punishable by fine or imprisonment, or both, under Section 1001 of Title 18 of the United States Code and that such willful false statements may jeopardize the validity of the document.

Date: January 7, 2002

Margo A. Milne

Full name of translator

Margo A. Milne

Signature of translator

107 W. Monroe St.

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Method for protecting metals against corrosion
and non-polluting reactive composition therefor

The present invention concerns novel macromolecular compounds, their synthesis and their use in mixture with a binder, particularly for paints usable for protecting metal surfaces against corrosion.

Polymers or copolymers bearing phosphonate groups or fluorine groups are already known. Substances of this kind, described more particularly in BE Pat. 09400881, are obtained from a halogenated polymer and/or copolymer activated by at least one peroxide and/or hydroperoxide function, to which at least one phosphonate chain is attached by means of an unsaturated monomer.

The substances described in said patent do protect metal surfaces, but they have many disadvantages.

A first disadvantage of the substances described in the prior art is they must be synthesized from a base material such as a halogenated polymer and/or copolymer of the type of poly(vinylidene fluoride) (PVDF), which is available commercially. Commercial chemicals, however, are highly elaborated and therefore very expensive, thus increasing the cost of the end product.

Another disadvantage is that the polymer and/or copolymer is thermoplastic and therefore sensitive to heat.

A third disadvantage is that activation techniques employing electron beams or ozone are onerous processes.

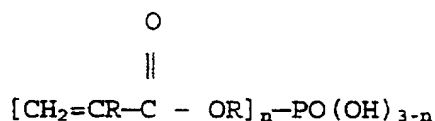
Yet another disadvantage is that with the materials described in the above-cited document, it is impossible to modulate the protection period of the metal.

In industry, protection for metal parts is desired as a temporary measure, prior to use, or for longer periods of time, depending on the subsequent use of the parts. For instance, it is desirable to be able to store protected parts for periods that can vary by a few months and then be able to use them.

Also known are polymers or copolymers bearing phosphonate groups, film-forming groups and crosslinkable groups.

The state of the art with regard to the synthesis of phosphorus-containing copolymers can be summarized as follows:

- phosphate monomers, which are acrylates of the following formula

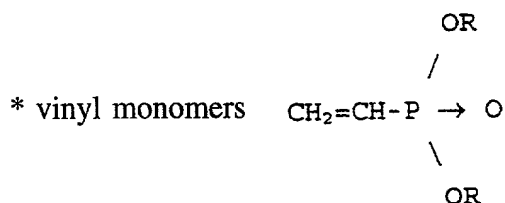


described in the patents

- * USP 5,378,291 (Nihon Parkerizing Co.),
- * PCT WO 88/02 382 (DuPont de Nemours),
- * EPA 0 221 498 (Johnson et Son),
- * EPA 0 376 591 (Rohm and Haas),
- * EPA 0 458 245 A1 (Nippon Paint Co.).

The disadvantages of these materials are, first, their instability with regard to hydrolysis (C—O—P bond) and the fact that their double-bond reactivity functionality is higher than 1, which naturally excludes them from the domain of solvated paints.

- phosphonated monomers, which are of several types:

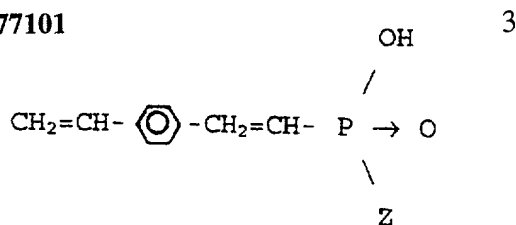


which are described in the patents:

- * DP 2 232 711 (Stauffer Chem.)
- * EPA 0 069 318 (Hoechst)

Their principal disadvantage, apart from price, is their very poor polymerization reactivity.

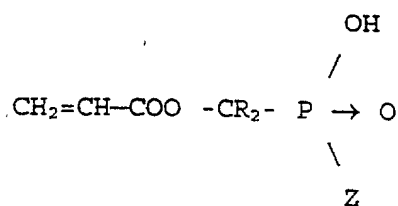
- styrene monomers:



which are described in US Pat. 3,051,740 (Monsanto).

The disadvantage of these materials is their intricate and costly synthesis.

- acrylate monomers



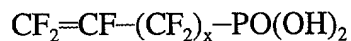
Z = R, OR

described in the patents:

- * EPA 0 278 029 (Dow Chemical)
- * USP 4,658,003 (Dow Chemical),

which may result in chemically unstable end products. In addition, the use and disposal of aldehydes, especially formol, which is a necessity for synthesis, are deprecated for environmental reasons.

- fluorophosphonates



described in the patent EPA 0 398 250 (Daikin).

Their disadvantages are poor radical-polymerization reactivity and very complex preliminary synthesis.

Ordinary paints are composed of a film-forming agent, which forms a film of one or more solvents, pigments and/or colorants on the metal and which hardens at ambient temperature or above. These paints are applied to the metal directly when it is free of oxidation, impurities and/or dirt or after it has undergone an anticorrosion treatment, for example phosphating followed by chromating. The chemicals used for such anticorrosion treatment contain toxic heavy-metal derivatives and highly volatile solvents. Such treatments are therefore harmful both to human health and to the environment.

The following patents can also be cited as belonging to the prior art:

- * EP 0 516 346, which describes a method for synthesizing certain telomers in an aqueous medium and provides for phosphorus-containing additives.
- * EP 0 277 711, which cites a few substituent phosphonic groups of polyesters somewhat randomly, without any specific intentions; moreover, it is primarily amines rather than phosphonates that are being sought.
- * EP 0 035 316, which alludes to mineral zinc phosphate additives rather than organic phosphonates.

The present invention concerns a treatment method and a composition that has the property of ensuring anticorrosion protection and adherence to metal but eliminates the need for prior treatment, particularly the anticorrosion treatments of phosphating and chromating.

To this end, the invention concerns a method for protecting metal articles against corrosion, characterized in that it consists in applying to the metal articles directly, i.e., without prior treatment of any kind, a composition formed, at the least, of a film-forming binder, at least one corrosion-inhibiting additive reactive with metal, and at least one oligomer additive bearing phosphonic acids.

According to other characteristics of this method:

- metal articles to be treated whose surfaces are excessively oxidized but not scaled are subjected to coarse brushing to reduce their surface oxidation to a low value that is not necessarily zero, and the composition is then applied to them;
- metal articles to be treated whose surfaces are excessively greasy are subjected to coarse cleaning to reduce their surface grease to a low value that is not necessarily zero, and the composition is then applied to them.

The invention also concerns a composition for protecting metal articles against corrosion, comprising a binder and at least one additive, characterized in that it comprises a film-forming binder, at least one corrosion-inhibiting additive reactive with metal, and at least one oligomer additive bearing phosphonic acids.

According to other characteristics of this composition:

- it further comprises one or more pigment additives;
- it further comprises one or more wetting agents;
- the wetting agent includes at least one component selected from the following:
 - => ethoxylated alkyl and aryl phosphonates,
 - => fluorocarbon derivatives,
 - => perfluoroalkylated ammonium sulfonate,
 - => perfluoroalkylated potassium sulfonate,
 - => perfluoroalkylated alcohol amino sulfonate
 - => perfluoroalkylated acrylate
- the additives bear a polymer chain compatible with the binder;
- the additives are statistical copolymers having blocks or grafts that bear sequences or grafted components compatible with the binder;
- the additives are copolymers of at least one monomer compatible with the binder and of at least one phosphonated monomer;
- the monomer compatible with the binder is chain-polymerizable and is selected from methacrylic acrylic, styrene, vinyl chloride, vinyl fluoride and vinyl ester monomers;

- the monomer compatible with the binder is selected from polycondensable monomers, diols and epoxide diacids;
- it includes phosphonic acid groups;
- the reactivity additive is a phosphonate or a phosphate whose molecular chains are either hydrocarbonated, fluorinated or chlorofluorinated;
- the reactivity additive includes at least one component selected from:
 - => alkyl acid phosphones and phosphonates,
 - => phosphoric acids,
 - => aminotrimethylene phosphonic acid,
 - => 1-hydroxyethylidene-1-1-diphosphonic acid,
 - => ethylene diamine tetramethylene phosphonic acid,
 - => hexamethylene diamine tetramethylene phosphonic acid,
 - => diethylene triamine pentamethylene phosphonic acid.

The invention will be better understood from the following detailed description, provided solely as an indicative and nonrestrictive example.

The following substances may be cited among those used in the formulations of the inventive composition:

A) Film-forming binders

These are homopolymers and copolymers obtained from unsaturated monomers used in paints. Said monomers are vinyl, acrylic, styrene, dienic, halogenated or nonhalogenated monomers well known to those skilled in the art.

In the case of reactive binders, the reactivity is most often supplied by carboxylic acid groups, but it can also be supplied by phosphonate groups, which makes the binders more compatible with the additives of the invention.

- The phosphonic groups are supplied by monomers that will be described below in connection with the reactive additives.

B) Reactive additives

These are molecular or macromolecular compounds of low molar mass (less than a few thousand, and preferably close to one thousand).

In addition, these additives all bear phosphorus-containing groups (preferably phosphonic groups), and their primary purpose is to react with metal at its surface. At least one acid function (P-OH) is therefore necessary.

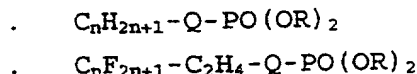
Three major classes of additives can be contemplated:

* Phosphonated alkanes or alkenes

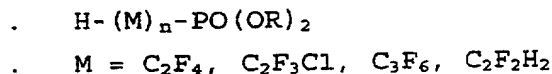
These substances have one or more phosphonic groups at their chain ends and/or within the chain.

The following formulas are possible:

- Monophosphonic compounds:

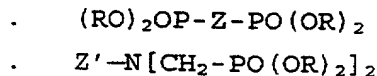


where Q = nil or $SC_x H_{2x}$ and $x = 2, 3$



R = H or alkyl in all cases.

- diphosphonic and telechelic compounds



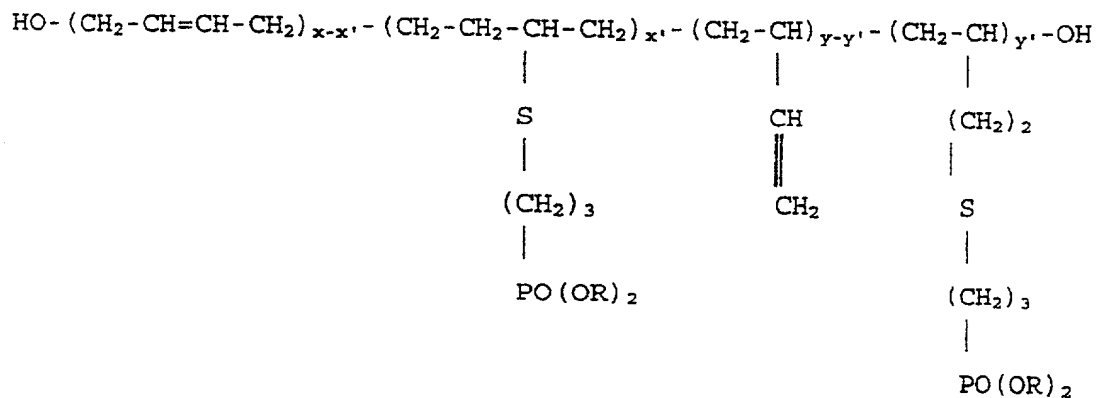
where: R = H, alkyl

Z' similar to the groups previously described with regard to monophosphonic compounds,

Z = alkylenes or arylene derived from nonconjugated dienes (divinylbenzene or 1-5-hexadiene, for example)

- polyphosphonic compounds:

Structures may contain plural phosphonic groups (≥ 2). For example, with PBHT as the starting material, the following formula is obtained:



where R = H or alkyl

References:

- Polymer Bulletin 41, 145-151 (1998),
- Grafting phosphonated thiol on hydroxy telechelic polybutadiene (Bernard Boutevin, Yves Hervaud, Gérard Moutedous) [citation sic].

* All-phosphonic statistical telomers and cotelomers

The structures are as follows, respectively:

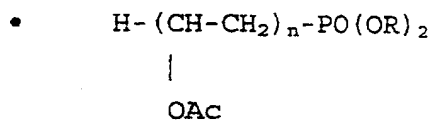


and

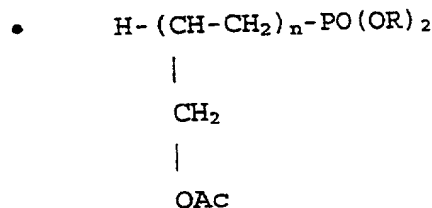


The phosphonic groups are supplied either by vinyl, allyl, acrylic or styrene monomers or by telogenic agents (R-X) of the phosphonate type (alkyl or haloalkyl).

The M_2 comonomers are all those generally used in copolymerization, which are well known to those skilled in the art; some examples are:

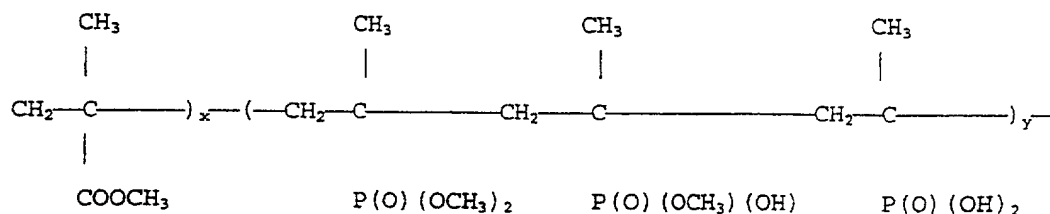


where R = H, alkyl from vinyl acetate



where R = H, alkyl from allyl acetate

- Starting with methyl methacrylate (MMA) and phosphonated methyl methacrylate (MAPHOS), radical seeding results, after hydrolysis, in statistical copolymers of the following formula:



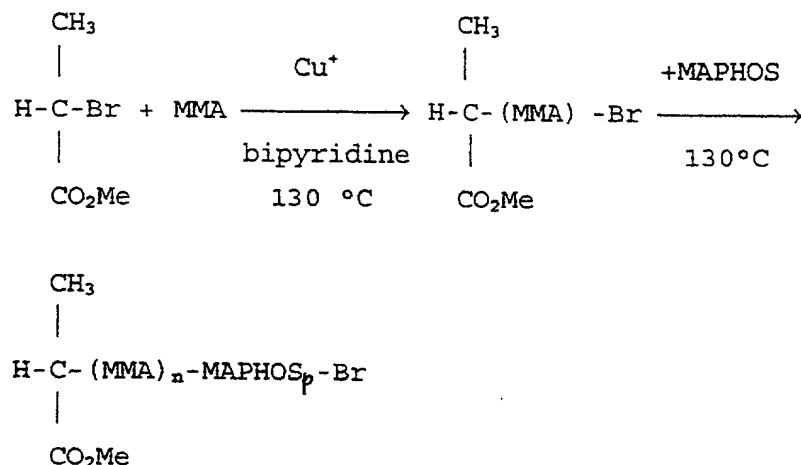
* Block phosphonic cotelomers.

Recent advances in controlled radical polymerization have provided access to block copolymers (see "Synthesis of Block Copolymers by Radical Polymerization and Telomerization," Advances in Polymer Science, Vol. 127, pp. 88-112, B. Améduri, B. Boutevin and Ph. Gramain, Ecole Nationale Supérieure de Chimie de Montpellier, URA 1193 CNRS 8, rue Ecole Normale, 34053 Montpellier Cedex France).

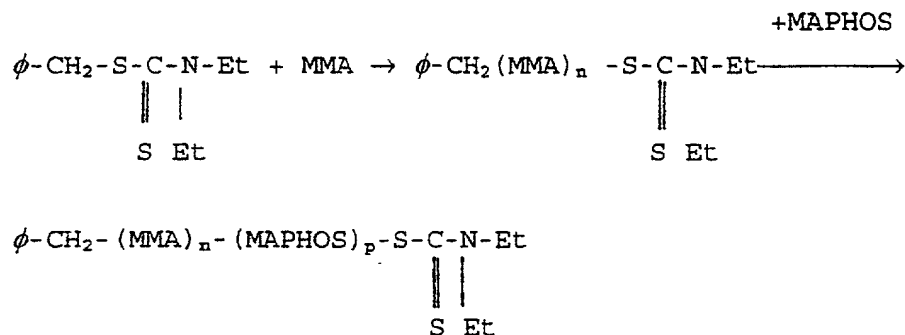
In the case of methacrylic derivatives, two methods have been used:

- atom-transfer radical polymerization (ATRP).

Example with MMA and MAPHOS:



- from thiuranes, cotelomers similar to the foregoing are obtained as follows:



(Living radical polymerization of MMA in the presence of piperidinodithiocarbamate derivatives as photoiniferters (cf. Denis Bertin, Bernard Boutevin, Philippe Gramain, Jean-Marc Fabre and Claude Montginoul

- Laboratoire de Chimie Appliquée, UPRES A 50760, Ecole Nationale Supérieure de Chimie de Montpellier - Laboratoire de Chimie Structurale Organique, UPRES A 50760, Université Montpellier II, Eup. Polym. J. Vol. 34, No. 1, pp. 85-90, 1998, Elsevier Science Ltd.)
[citation sic]

C) Anticorrosion additives

- modified zinc, calcium or strontium orthophosphate,
- modified zinc or aluminum orthophosphate,
- modified organic zinc orthophosphate,
- modified zinc or molybdenum orthophosphate,
- phosphate, zinc silicate, modified hydrated aluminum,
- modified zinc, calcium, aluminum or strontium polyphosphate,
- etc.

D) Other additivesMineral pigments:

Aluminum, mica, glass flakes, talc, titanium oxide, iron oxides, barium sulfate, chrome green, graphite, silicas, silicates, etc.

Organic pigments:

Quinacridones, pyrazolone, isonidoline, quinophthalone, phthalocyanine, indatone, etc.

SURFACTANTS:

- ethoxylated alkyl and aryl phosphates,
- fluorocarbon derivatives,
- perfluoroalkyl ammonium sulfonate,
- perfluoroalkyl potassium sulfonate,
- perfluoroalkyl aminoalcohol sulfonate,
- perfluoroalkyl acrylate.

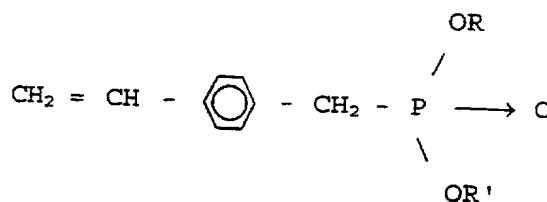
The invention will be better understood from the following detailed description, provided solely as an indicative and nonrestrictive example.

The invention simplifies the use of paints and coatings and utilizes synergies among the properties of the binders and additives used. In particular, if the binder has good barrier properties and the additive has very good adherence to metal, the resulting materials have excellent corrosion-resistance properties.

Since interpolymer compatibility is a relatively rare characteristic, the polymers that are combined are of the same kind or are very similar, i.e., differing with respect to molecular size or composition, which in most cases is related to the composition of the binder, although they can have some new units.

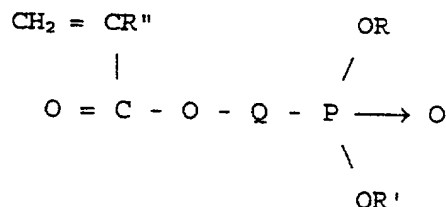
Phosphonated monomers bear a polymerizable double bond and a phosphonic group, joined to the side chain of the monomer by a C-P bond. Similarly, polycondensable monomers have a phosphonate group connected to the side chain of the monomer by a C-P bond.

Examples include styrene monomers of the formula:



in which R and R' are similar or different and equal.

Other examples that can be cited are acrylic monomers of the formula:



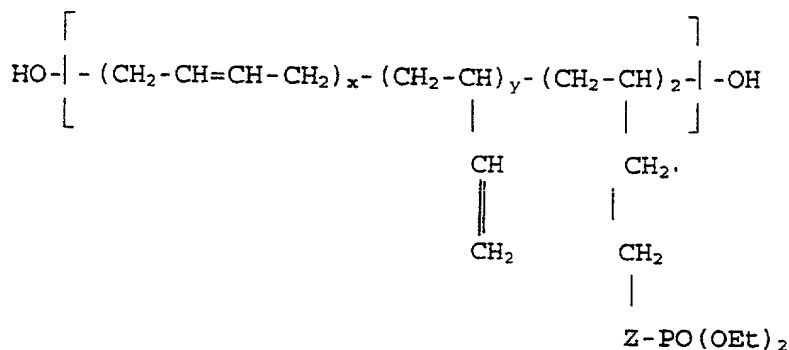
in which R and R' are similar or different.

Q=

- $\text{CH}_2 - \text{CH}_2$
- $(\text{CH}_2)_2 - \text{S} - (\text{CH}_2)_3$
- $\text{CH}_2 - \text{CH}(\text{OH}) - \text{CH}_2 - \text{O} - \text{C}(=\text{O}) - \text{CH}_2 - \text{S} - (\text{CH}_2)_3$

- $\text{CH}_2 - \text{C}(\text{CH}_3)$
|
OH
- $\text{CH}_2 - \text{CH} - \text{CH}_2$
|
OH

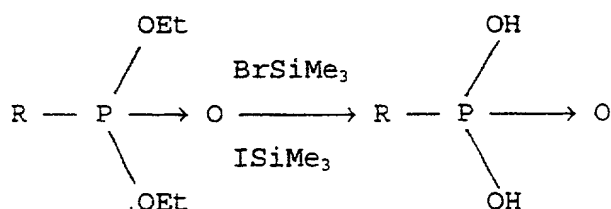
Reaction additives can also be obtained by the chemical modification of commercial oligomers such as PBHT, from Atochem,



where Z = nil or S-CH₂-CH₂.

All the phosphonated additives described above are effective only in acid form.

The chemical transformation of phosphonic esters, whether on monomers or on copolymers, is well known to those skilled in the art and can be performed, in an acidic or basic medium, to obtain phosphonic monoacids, or, using halosilanes, to prepare phosphonic diacids according to the following reaction:



REPLACEMENT SHEET (RULE 26)

The following description, provided in regard to nonrestrictively annexed examples, will furnish a better understanding of how the invention can be put to use.

Example 1:

Synthesis of a 55/45 MMA/MAPHOS copolymer

Let MMA represent methyl methacrylate $\text{CH}_2=\text{C}-\text{CO}_2\text{CH}_3$
 CH_3
 and MAPHOS phosphonated methacrylate $\text{CH}_2=\text{C}-\text{CO}_2(\text{CH}_2)_2\text{PO}(\text{OCH}_3)_2$
 prepared according to the method described by C. Brondino (Thesis, Montpellier, 1996).

A one-liter three-necked flask provided with a water-based coolant, nitrogen bubbling and a dropping funnel was charged with 20.0 g (0.2 mol) of MMA, 44.4 g (0.2 mol) of MAPHOS and 400 ml of THF. The dropping funnel was charged with 1.968 g of AIBN [2,2'-azobisisobutyronitrile] dissolved in 100 ml of THF.

The reaction mixture was degassed for 15 min and heated to 70°C. 30 ml of seeding solution were then added dropwise. Two hours later, another 30 ml of seeding solution were added dropwise. The rest of the seeding solution was then added dropwise after 4 h.

After 6 h of reaction, the reaction mixture was precipitated in 4 l of pentane. The copolymer thus collected was filtered and was then dissolved in 200 ml of dichloromethane. The mixture was again precipitated in 4 l of pentane, and after filtration a fine, white, dusty, very hygroscopic powder was obtained. This was dried in a balloon flask under high vacuum for 4 h. 59.8 g of copolymer was obtained, for a yield of 93%.

^1H NMR analysis (CDCl_3) confirmed the composition of the copolymer, which contained 54% MMA and 46% MAPHOS.

Example 2:

Hydrolysis of a 55/45 MMA/MAPHOS copolymer

A one-liter three-necked flask provided with a water-based coolant, nitrogen bubbling and a dropping funnel was charged with 59.8 g (0.37 mol) of the copolymer from Example 1, dissolved in 500 ml of dichloromethane. The solution was degassed for 15 min; this was followed

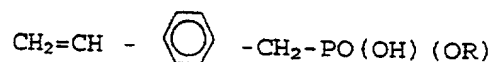
by the dropwise addition of 53 ml (0.41 mol) of bromotrimethylsilane freshly distilled under nitrogen. The mixture was stirred at ambient temperature for 3 h.

At the end of the reaction, the solvent was evaporated with a Rotavapor, and an excess of methanol (500 ml) was then added. The mixture was stirred at ambient temperature for 3 h and the solvent was evaporated again. The end product collected was 58.8 g of hydrolyzed copolymer in the form of a yellowish paste.

Example 3:

Synthesis of an MMA/phosphonated styrene copolymer

Let MMA stand for methyl methacrylate, the formula for phosphonated styrene being:



R = Et, $\text{H}_2\text{N}^+(\text{C}_6\text{H}_{11})_2$

These substances have already been described. See Bernard Boutevin*, Bachar Hamoui, Jean-Pierre Parisi and Bruno Ameduri, "Homopolymerization and copolymerization of salt formed from a new diethyl styrenic phosphonate monomer," *Eur. Polym. J.* 32/2 (1996), 159-163, Copyright © 1996, Elsevier Science Ltd., printed in Great Britain, All rights reserved, 0014-3057(95)00132-8 - 0014-3057/96, \$15.00 + 0.00.

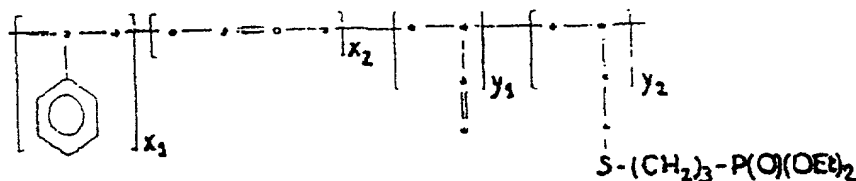
Example 4:

Grafting of phosphonated thiol, $\text{HS}-(\text{CH}_2)_3-\text{PO}(\text{OEt})_2$, on a styrene-butadiene copolymer

A 3-liter flask was charged with 10 g of Finapren 502, 2.76 g of phosphonated thiol and 0.1 g of benzophenone, the whole dissolved in 700 ml of THF. The solution was degassed with nitrogen for 15 min and the reaction mixture was irradiated with UV for 24 h.

The solution was found to have formed a gel, which was redissolved in a total volume of THF of 2.5 l. At the end of the reaction, the solution was concentrated to 700 ml and precipitated in 4 l of methanol. The white precipitate collected was filtered, rinsed and dried under vacuum. This resulted in isolation of the grafted polymer in the form of an elastic gum.

^1H NMR analysis (CDCl_3) confirmed the structure of the expected material.



Elementary analysis was used to determine the percentage of phosphorus in the grafted copolymer. The value in this case was 2%. The grafting efficiency was therefore 50%.

Example 5:

Synthesis of a copolymer containing an epoxide group

A 3.5-liter autoclave equipped with a stirrer was charged with 2 l of acetonitrile, 1 mol 2-hydroxyethyl vinyl ether, 4 mol 2-(dimethoxyphosphonate) ethyl vinyl ether and 22 g of benzoyl peroxide. The mixture was degassed under vacuum and 5 mol chlorotrifluoroethylene were added. The mixture was heated to 95°C, causing the pressure to increase to 30 bars. The pressure had fallen to 10 bars at the end of 6 h. The reactor was cooled and was degassed to remove the unreacted chlorotrifluoroethylene. A copolymer solution was obtained that yielded nearly 38% dry extract. This copolymer contained fluorine motifs supplying 19 to 21% fluorine (elementary analysis).

Example 6:

Synthesis of the copolymer from Example 5 with silyl groups

A 3-liter reactor was charged with 160 g of the copolymer obtained according to Example 5, in acetonitrile, and containing 0.5 mole-equivalent of $\text{OP}(\text{OCH}_3)_2$. One mole of bromotrimethylsilane was added at ambient temperature during 2 h. After reaction and evaporation of the solvent, proton nuclear magnetic resonance ($^1\text{H-NMR}$) revealed $\text{O-Si}(\text{CH}_3)_3$ groups on the copolymer, substituted for the OCH_3 groups.

This polymer can be stored as is, or it can be hydrolyzed with excess methanol. The latter method yields a copolymer containing acid phosphonate structural units: $-\text{PO}(\text{OH})_2$.

Example 7:

The reactor was charged with 160 g of the copolymer from Example 5 and one mole of chlorotrimethylsilane was added in place of the bromotrimethylsilane. The majority component obtained was the phosphonate derivative bearing a methyl-ester function and a silyl function. After hydrolysis, the resulting copolymer contained mixed phosphonate acid-ester structural units of the formula: $-\text{PO}(\text{OCH}_3)(\text{OH})$.

Example 8:Synthesis of the ammonium salt of the copolymer from Example 6

The reactor was charged with 140 g of the copolymer obtained according to Example 2, containing approximately 0.5 mole-equivalent of $-\text{PO}(\text{OH})_2$; to this was added one mole of cyclohexylamine, i.e., 181 g, and the mixture was left to react for one hour. Infrared analysis of the product demonstrated disappearance of the OH bands.

Example 9:

The reactor was charged with the same constituents as in Example 5, but one mole of chlorotrifluoroethylene was replaced with one mole of $\text{CH}_2=\text{CH}-\text{O}-(\text{CH}_2)_2-\text{C}_8\text{F}_{17}$.

The reaction was then carried out under the same conditions as in Example 5. The end product had a fluorine concentration, determined by elementary analysis, of about 31%. This copolymer can be treated by the same method as that of Examples 6 to 8.

Example 10:

The compounds were synthesized according to Examples 5 to 8, but the hydroxyethyl vinyl ether was replaced with dimethoxy-methylsilylpropyl vinyl ether of the formula $\text{CH}_2=\text{CH}-\text{O}-(\text{CH}_2)_3-\text{Si}(\text{CH}_3)(\text{OCH}_3)_2$.

Example 11:

A reactor was charged with approximately 180 g of the copolymer according to Example 10 and containing 0.5 mole-equivalent of $-\text{PO}(\text{OCH}_3)_2$. One mole chlorotrimethylsilane was added and the mixture was left to react for two hours at ambient temperature. As in Examples 2 and 3, ^1H NMR then revealed a signal indicating the presence of $\text{OSi}(\text{CH}_3)_3$ groups.

Example 12:

Under the same operating conditions as in Example 5, the reactor was charged with a mixture composed of one mole of allyl alcohol and one mole of allyl diethylphosphonate. After cooling, to this was added a gaseous mixture composed of vinylidene fluoride and chlorotrifluoroethylene in a ratio of 6.5:1.5. Under the same pressure conditions as in Example 5, after 6 h of reaction and degassing, a fluorinated copolymer was obtained whose fluorine concentration, measured by elementary analysis, was about 40%.

Example 13:

Under the same operating conditions as in Example 5, the reactor was first charged with a mixture composed of 1 mol allyl hydroxyethyl ether and 1 mol diethyl vinylphosphonate. After degassing and cooling, 6 mol vinylidene fluoride and 2 mol hexafluoropropylene, $\text{CF}_3\text{--CF=CF}_2$, were added. After 5 h of reaction, a copolymer containing approximately 48% fluorine was obtained.

Example 14:

Under the operating conditions of Example 5, the reactor was first charged with 1 mol diethyl allylphosphonate, 1 mol allyl alcohol and 1 mol vinyl acetate.

After cooling and degassing, 6 mol chlorotrifluoroethylene were added. After 6 h of reaction, a copolymer containing approximately 31% fluorine was obtained.

Example 15:

A Hastelloy autoclave reactor with a capacity of 1000 ml was charged with:

- 234 g (1.69 mol) of phosphonate, $\text{HPO}(\text{OEt})_2$
- 2.5 g ($1.71 \cdot 10^{-2}$ mol) of di-*tert*-butyl peroxide,
- 200 g (4.93 mol) of acetonitrile

and 108 g (1.69 mol) of vinylidene fluoride (VF_2).

Five hours of reaction at 140°C yielded a telomer mixture $\text{H}(\text{--CF}_2\text{--CH}_2)_n\text{--PO}(\text{OEt})_2$ with a DP_n of about 3.0 and a VF_2 conversion ratio on the order of 90%.

Example 16:

Under the same conditions described in Example 15, the reaction was carried out with chlorotrifluoroethylene (CTFE). 1.97 g (1.69 mol) of CTFE were added. The telomer mixture obtained, $\text{H}-(\text{CFCl}-\text{CF}_2)_n-\text{PO}(\text{OEt})_2$, had a DP_n of about 2, and the CTFE conversion ratio was 78%.

Example 17:

In accordance with Example 15, the phosphonate was dimethyl hydrogen phosphonate, $\text{HPO}(\text{OCH}_3)_2$.¹

Example 18:

In accordance with Example 16, the phosphonate was dimethyl hydrogen phosphonate, $\text{HPO}(\text{OCH}_3)_2$.¹

Example 19:

The substances from Example 15 were hydrolyzed, either by means of methanol after silylation by a halosilane of the type $\text{XSi}(\text{CH}_3)_2$, where $\text{X} = \text{Cl}, \text{Br}$, or by the action of hydrochloric acid.

Thus, commencing with 50 g of $\text{HCF}_2-\text{CH}_2-\text{PO}(\text{OEt})_2$ monoadduct and 39.4 g of $\text{BrSi}(\text{CH}_3)_3$ added dropwise in the presence of CH_2Cl_2 (solvent) and after 2 h of agitation, 50 ml of methanol were added to the medium. After distillation, 34.7 g of a monoacidic substance, $\text{H}-\text{CF}_2-\text{CH}_2-\text{PO}(\text{OH})(\text{OEt})$, were obtained.

Example 20:

The substances from Example 16 were hydrolyzed as described in Example 19.

A 100-ml balloon flask provided with a coolant was charged with 4.00 g ($1.57 \cdot 10^{-2}$ mol) of monoadduct dissolved in 20 ml of toluene, to which were added 8 ml of 12N HCl ($9.6 \cdot 10^{-2}$ mol; 6 eq. of HCl to 1 eq. of ester). The solution was maintained at solvent reflux (120°C) for 12 h.

After cooling of the solution, the toluene was evaporated and the solution was washed twice with 50 ml of distilled water. It was reconcentrated. A white solid weighing 4.44 g was

¹TRANSLATOR'S NOTE: Discrepancy in formulas sic; the subscript "2" is missing in the first occurrence.

recovered from the aqueous phase after concentration and oven-drying. NMR analyses revealed cleavage of 75% of the "phosphonic ester" groups.

Example 21:

A 100-ml flask provided with a coolant was charged with 6 g of PBHT R-20, 4 g of thiol HS-(CH₂)₃-PO(OEt)₂, 0.18 g of AIBN and 60 g of THF (solvent). After 4 h of reaction at 70°C and after treatment of the product, NMR analyses revealed a grafting ratio of 19%. The grafted product therefore contained 2.6% phosphorus. These reactions have already been described:

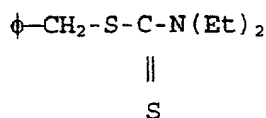
Ref.: Bernard Boutevin, Yves Hervaud and Gérard Molédous, "Grafting phosphonated thiol on hydroxy telechelic polybutadiene," *Polymer Bulletin* 41 (1998), 145-151.

Example 22:

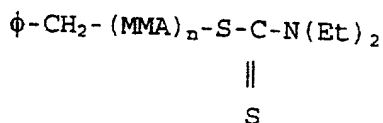
Synthesis of the MMA/MAPHOS block copolymer.

Step 1:

MMA was polymerized with thiuram.



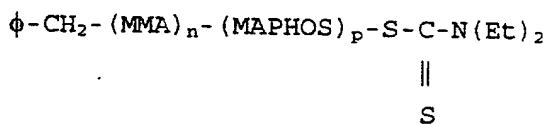
The result was compound (A), of the formula:



with a number molecular weight of approximately 20,000.

Step 2:

Photochemical polymerization of compound (A) was performed with MAPHOS, yielding copolymer (B) of the formula:



7 MAPHOS per chain were added (p therefore equalled 7).

The number molecular weight was approximately 21,000 (structure checked by NMR).

Step 3:

Compound 3 was hydrolyzed by means of $\text{BrSi}(\text{Me})_3$, then CH_3OH .

Example 23:

A 1000:1:2 mixture of styrene, dicumyl peroxide and "Tempo" (piperidine nitroxyl) was introduced.

The mixture was maintained at 120°C for 8 h. An aliquot was analyzed by GPG (gel permeation chromatography), which revealed the formation of a polystyrene with a molecular weight of 45,000, fairly close to the expected value of 50,000.

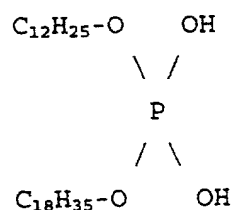
To the reaction mixture was added $\text{CH}_2=\text{CH}-\phi-\text{CH}_2-\text{PO}(\text{OC}_2\text{H}_5)_2$, in molar proportions of 1 mol polystyrene to 100 mol phosphonated monomer. The mixture was maintained at 120°C for 10 h, resulting in complete conversion to a phosphonated styrene derivative.

The final polystyrene equivalent molecular weight was 68,000. ^1H NMR confirmed the presence of about 5 styrene motifs to 1 phosphonate motif (integration of the $-\text{O}-\text{CH}_2-\text{CH}_3$ group) with respect to all aromatic protons.

The esters were hydrolyzed with ClSiMe_3 to obtain the corresponding diacid.

Example 24:

Synthesis of crosslinkable phosphonates of the following formula



The alcohol $\text{C}_{12}\text{H}_{25}\text{OH}$ was added mole by mole to POCl_3 in chloroform in the presence of triethylamine to trap the hydrochloric acid formed. After two hours of reaction, the unsaturated alcohol $\text{C}_{18}\text{H}_{35}\text{OH}$ was added, and after two hours of reflux in CHCl_3 , the mixture was hydrolyzed. After extraction, a monoacid with an acid index corresponding to the above

formula was isolated.

Any of the following three preparations can be used for this example:

Preparation A

From the compound obtained in Example 24, an aqueous solution of the following composition is prepared:

10 parts compound of Example 24

1 part nonyl phenoxyacetic acid

a sufficient quantity of ethanolamine to yield $8.5 \leq \text{pH} \leq 9.5$

6 parts propylene glycol monomethyl ether

water to make 100 parts.

This solution was applied to steel surfaces, and after removal of the water, protection in accordance with ASTM Standard D 1735-62 was obtained on exposure to a moisture-saturated atmosphere at 37.8°C. The corrosion in accordance with ASTM Standard D 610-68 was estimated at Grade 10 after one week. This was equivalent to a complete absence of corrosion, whereas a steel specimen not treated in this manner exhibited Grade 1 corrosion, corresponding to corrosion of 50% of the surface, after only 24 h.

The compound according to Example 24 provides temporary protection for 168 h, since it is not crosslinked. It can be removed from the steel to make way for subsequent treatment, for example the steel can be rolled, formed, transformed by cutting, stamping, welding, etc.

Preparation B

5 parts compound of Example 24

5 parts 50% styrene-acrylic copolymer

1 part nonyl phenoxyacetic acid

dimethylaminoethanol in sufficient quantity to yield $8.5 \leq \text{pH} \leq 9.5$

6 parts propylene glycol monomethyl ether

water to make 100 parts

This composition resulted in Grade 10 on galvanized steel after six weeks of exposure. Without treatment, an identical surface showed Grade 1 corrosion after one week of exposure.

Preparation C

5 parts compound of Example 13

5 parts 50% styrene-acrylic copolymer

1 part nonyl phenoxyacetic acid

cyclohexylamine in sufficient quantity to yield $8.5 \leq \text{pH} \leq 9.5$

2 parts substituted imidazole formiate

6 parts propylene glycol monomethyl ether

water to make 100 parts

Under the same test conditions as in Example 20, when applied to galvanized steel, this composition resulted in Grade 10 after ten days of exposure.

Using the same composition, the corrosion test was performed by immersion in a 3.5% NaCl solution: without protection, corrosion was evident on a bare steel surface after 15 min of immersion; after the composition had been applied, no corrosion whatsoever was observed after 12 h of exposure.

This composition is a one that affords temporary protection and can easily be removed by washing.

Example 25:

Epoxidation of the salt of the acid obtained according to Example 13.

To one mole of acid from Example 1 were added one mole of ammonia followed by 1.2 mol *p*-chloroperbenzoic acid, and reflux was maintained for one hour. The mixture was concentrated to 50% dry extract.

Example 26:

To the mixture obtained according to Example 14, acrylic acid was added mole by mole and reflux was maintained for 8 h. After the addition of 1% hydroquinone, an acrylated substance was obtained.

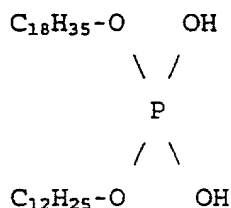
Example 27:

Diethyl hydrogen phosphonate, $\text{HPO}(\text{OEt})_2$, was added to 1-dodecene according to the method described by Peleprat et al. The compound $\text{C}_{12}\text{H}_{25}\text{PO}(\text{OEt})_2$ was obtained in a yield of

This compound was hydrolyzed with bromotrimethylsilane according to the method described by Hamoui et al. (Macromol. Chem. Phys., 1985, 1995 [citation sic]).

$C_{12}H_{25}PO(OH)_2$ was obtained in this manner.

This diacid was esterified in toluene under heat with a Dean Stark system to remove the water, the esterification being done with an alcohol of the formula $C_{18}H_{35}OH$, to yield a compound of the following formula:

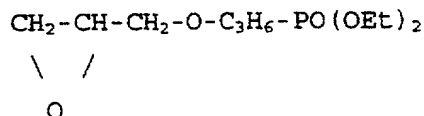


This compound was epoxidized as in Example 14, and acrylation was then performed as in Example 25.

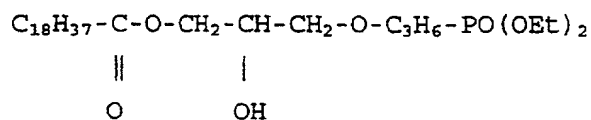
Example 28:

As in Example 16, diethyl hydrogen phosphonate, $HPO(OEt)_2$, was added to one mole of allyl glycidyl ether.

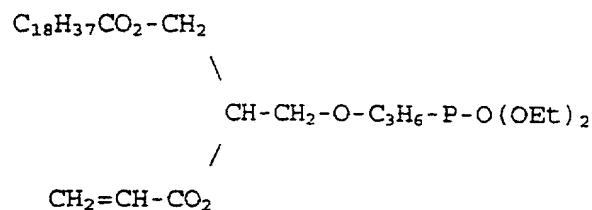
The following compound was obtained quantitatively:



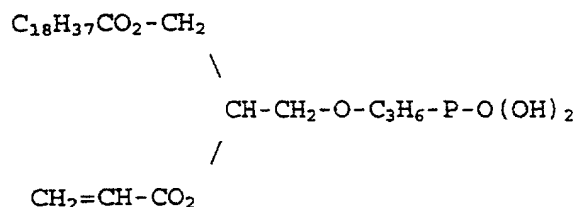
The fatty acid $C_{18}H_{37}CO_2H$ was added to this epoxide in the presence of 10^{-2} mol ethyl laurylamine to yield a compound of the following formula:



To the preceding compound was added acryloyl chloride, and a compound of the following formula was obtained:



which, when hydrolyzed with bromotrimethylsilane, quantitatively yielded the corresponding acid, of the following formula:



Either of the following two compositions can be used for long-term protection on bare steel:

Preparation A

- 145 parts compound obtained in Example 28
- 220 parts polyvinyl difluoride grafted with hydroxyethyl acrylate
- 6 parts ammonia
- 167 parts rutile (titanium oxide)
- 33 parts red iron oxide
- 2.5 parts dispersant
- 33 parts diethylene glycol
- 2.5 parts antifoaming agent
- 68 parts melamine methylol
- 323 parts water

The characteristics of the composition are as follows:

$$8.6 \leq \text{pH} \leq 8.8$$

ratio of pigment to grafted polyvinyl difluoride = 0.55:1.0

Ford No. 4 viscosity = 45/50 seconds

% melamine: dry extract: 18.6

The composition is applied by spraying or after dilution.

The coating is baked for 10 min at 180°C or 15 min at 150°C. The resultant coating has a protection period of 500 h (resistance to saline mist measured according to AFNOR Standard x 41.002).

The pencil hardness is F.2H.

The NFR 30038 adherence is 100%.

Preparation B

6 parts compound obtained in Example 28

5 parts vinyl-maleic copolymer

4 parts 9% polyvinyl alcohol

ammonia in sufficient quantity to yield $8.5 \leq \text{pH} \leq 9.0$

1 part hydroxyethyl cellulose

1 part HLB 12 nonionic wetting agent

8 parts $\text{Zn}_3(\text{PO}_4)_2 \cdot 2\text{H}_2\text{O}$

water to make 100 parts

The density of the composition is 1.08 to 1.10.

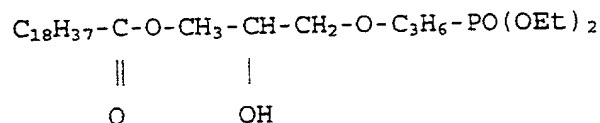
The Ford No. 4 viscosity is 20 to 22 seconds.

The composition is sprayed on or applied as is.

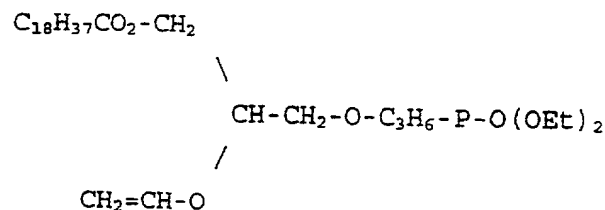
Baking is performed for 15 min at 150°C. Long-term protection of steel is obtained, with a protection period of more than 500 h.

Example 29:

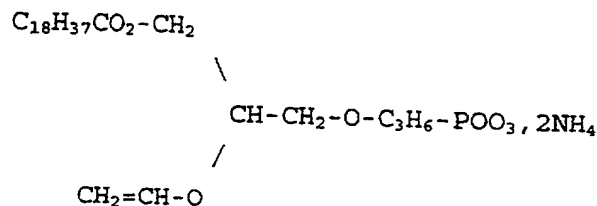
Commencing with the alcohol obtained in Example 17,



transvinylation was performed with butyl vinyl ether, using a palladium-containing catalyst as described in *J. of Phys. Chem.* 44 (1989), 395, to yield the compound of the following formula:



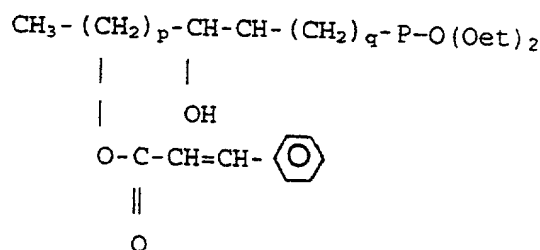
This compound was hydrolyzed with $\text{BrSi}(\text{Me})_3$ and ammonia to yield the disalt of the following formula:



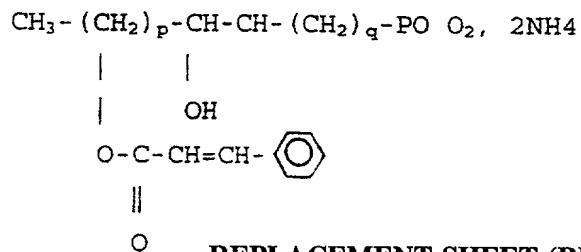
Example 30:

To the epoxide prepared in Example 14, cinnamic acid was added according to the method of Example 15.

A substance having the following formula was obtained:



Hydrolysis, performed as hereinabove, yielded a compound of the following formula:



REPLACEMENT SHEET (RULE 26)

A composition according to the invention can also be in the form of an aqueous emulsion:

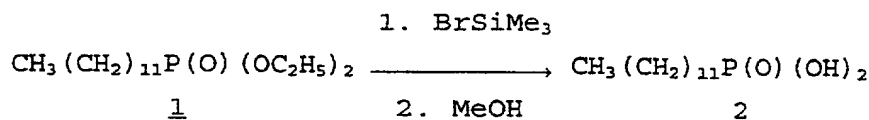
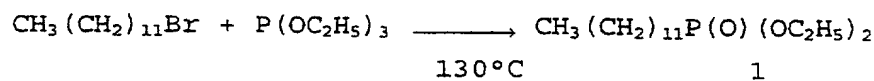
Example 31:

An aqueous emulsion of polyethylene was prepared from the following constituents:

	Parts
PE-AA AC 5120 copolymer	40
25% ammonia solution	8
Dodecylphosphonic acid	4
Xanthan gum	1
Demineralized water	197

Synthesis of dodecylphosphonic acid

Dodecylphosphonic acid was prepared in two steps as follows:



A three-necked flask provided with a dropping funnel, an argon inlet and a distilling apparatus was charged with 49.8 g of bromododecane. The assembly was placed in an inert atmosphere and heated to 130°C. 36.5 g of triethyl phosphite were then added dropwise through the funnel. After 24 h of reaction, the remaining reactants were removed by distillation under vacuum, resulting in the collection of 55.1 g of diethyl dodecylphosphonate 1, i.e., a yield of 90%.

30.6 g of Compound 1 isolated in this manner were then dissolved in 500 ml of dichloromethane. 30.6 g of bromotrimethylsilane (2 eq.) were then added in an inert atmosphere. The mixture was stirred at ambient temperature for 3 h. The solvent was then evaporated, after which 500 ml of methanol were added. After 2 h of stirring at ambient

temperature, the methanol was evaporated. A white solid was collected and was washed in ether and dried under vacuum. 23.9 g of dodecylphosphonic acid 2 were collected, for a yield of 95.6%.

Preparation of the aqueous emulsion of polyethylene

A pressurized reactor was charged with Ethylene-Acrylic Acid copolymer AC5120, 25% ammonia solution and demineralized water. All these components were heated to 110° for 15 min with vigorous mechanical agitation. The mixture was cooled rapidly in ice and the emulsion was then collected in the form of a completely homogeneous slurry with a pH of 10.

The aqueous emulsion of polyethylene was placed in a mechanical agitator. Under gentle agitation, xanthan gum was added, followed by dodecylphosphonic acid. The agitation speed was gradually increased to dissolve the additives fully in the emulsion.

CLAIMS

1. A method for protecting metal articles against corrosion, characterized in that it consists in applying to the metal articles directly, i.e., without prior treatment of any kind, a composition formed, at the least, of a film-forming binder, at least one corrosion-inhibiting additive reactive with metal, and at least one oligomer additive bearing phosphonic acids.

2. The method of claim 1, characterized in that metal articles to be treated whose surfaces are excessively oxidized but not scaled are subjected to coarse brushing to reduce their surface oxidation to a low value that is not necessarily zero, and the composition is then applied to them.

3. The method of claim 1, characterized in that metal articles to be treated whose surfaces are excessively greasy are subjected to coarse cleaning to reduce their surface grease to a low value that is not necessarily zero, and the composition is then applied to them.

4. A composition for protecting metal articles against corrosion, comprising a binder and at least one additive, characterized in that it includes a film-forming binder, at least one corrosion-inhibiting additive reactive with metal, and at least one oligomer additive bearing phosphonic acids.

5. The composition of claim 4, characterized in that it further includes one or more pigment additives.

6. The composition of claim 4, characterized in that it further includes one or more wetting agents.

7. The composition of claim 4, characterized in that it contains a wetting agent formed of at least one component selected from the following:

- => ethoxylated alkyl and aryl phosphonates,
- => fluorocarbon derivatives,
- => perfluoroalkylated ammonium sulfonate,
- => perfluoroalkylated potassium sulfonate,

=> perfluoroalkylated amino alcohol sulfonate,

=> perfluoroalkylated acrylate.

8. The composition of claim 4, characterized in that said additives each bear a polymer chain compatible with the binder.

9. The composition of claim 8, characterized in that said additives are statistical copolymers having blocks or grafts that bear sequences or grafted components compatible with the binder.

10. The composition of claim 8, characterized in that said additives are copolymers of at least one monomer compatible with the binder and of at least one phosphonated monomer.

11. The composition of claim 8, characterized in that said monomer compatible with said binder is chain-polymerizable and is selected from methacrylic acrylic, styrene, vinyl chloride, vinyl fluoride and vinyl ester monomers.

12. The composition of claim 8, characterized in that said monomer compatible with said binder is selected from polycondensable monomers, diols and epoxide diacids.

13. The composition of claim 8, characterized in that it includes phosphonic acid groups.

14. The composition of claim 4, characterized in that the reactivity additive is a phosphonate or a phosphate whose molecular chains are either hydrocarbonated, fluorinated or chlorofluorinated.

15. The composition of claim 14, characterized in that said reactivity additive includes at least one component selected from:

=> alkyl acid phosphones and phosphonates,

=> phosphoric acids,

=> aminotrimethylene phosphonic acid,

=> 1-hydroxyethylidene-1-1-diphosphonic acid,

=> ethylene diamine tetramethylene phosphonic acid,

=> hexamethylene diamine tetramethylene phosphonic acid,

=> diethylene triamine pentamethylene phosphonic acid.

Declaration and Power of Attorney For Patent Application

English Language Declaration

As a below named inventor, I hereby declare that:

My residence, post office address and citizenship are as stated below next to my name,

I believe I am the original, first and sole inventor (if only one name is listed below) or an original, first and joint inventor (if plural names are listed below) of the subject matter which is claimed and for which a patent is sought on the invention entitled

METHOD FOR PROTECTING METAL AGAINST CORROSION AND NON-POLLUTING REACTIVE COMPOSITION THEREFOR

the specification of which (check one):

☐ is attached hereto.

☐ was filed on _____ as Application Serial No. _____ and was amended on _____ (if applicable).

I hereby state that I have reviewed and understand the contents of the above-identified specification, including the claims, as amended by any amendment referred to above.

I acknowledge the duty to disclose information which is material to patentability as defined in Title 37, Code of Federal Regulations, § 1.56.

I hereby claim foreign priority benefits under Title 35, United States Code, §119 of any foreign application(s) for patent or inventor's certificate listed below and have also identified below any foreign application for patent or inventor's certificate having a filing date before that of the application on which priority is claimed:

<u>Prior Foreign Applications</u>			<u>Priority Claimed</u>	
<u>PCT/FR00/01636</u> (Number)	<u>PCT</u> (Country)	<u>13/06/00</u> (Day/Month/Year Filed)	Yes [X]	No []
<u>99/07440</u> (Number)	<u>France</u> (Country)	<u>11/06/99</u> (Day/Month/Year Filed)	Yes [X]	No []

I hereby claim the benefits under Title 35, United States Code, §119(e) of the following United States Provisional Application:

		<u>Priority Claimed</u>	
<u> </u> (Number)	<u> </u> (Day/Month/Year Filed)	Yes []	No []

I hereby claim the benefit under Title 35, United States Code, §120 of any United States application(s) listed below, and insofar as the subject matter of each of the claims of this application is not disclosed in the prior United States application in the manner provided by the first paragraph of Title 35, United States Code, §112, I acknowledge the duty to disclose information which is material to patentability as defined in Title 37, Code of Federal Regulations, §1.56 which became available between the filing date of the prior application and the national or PCT international filing date of this

application.

This application is a _____ of U.S. Application

Serial No.	Filing Date	Status (Patented, Pending, Abandoned)
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I hereby declare that all statements made herein of my own knowledge are true and that all statements made on information and belief are believed to be true; and further that these statements were made with the knowledge that willful false statements and the like so made are punishable by fine or imprisonment, or both, under Section 1001 of Title 18 of the United States Code and that such willful false statements may jeopardize the validity of the application or any patent issued thereon.

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